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The PIXE analysis using an external proton beam have been investigated at Kyoto University cyclotron. Here discussed is the usefulness of the external beam PIXE as an analytical tool in the study of elements. A detection limit of 7×10^{-8} g for iron was obtained. Examples of applications of PIXE to environmental, biological, archaeological and electrochemical problems are given.

KEY WORDS: PIXE analysis / Element analysis / Nondestructive analysis

I. INTRODUCTION

PIXE (Proton Induced X-ray Emission) has become widely used in the trace element analysis. It is a powerful analytical tool for a variety of reasons: — It is a nondestructive and highly sensitive multielement analysis, and it requires only small amounts of sample. The good review for this method can be found elsewhere in the literatures.[1)]

In PIXE analysis normally the sample is placed in vacuum. However, in case of the routine PIXE analysis it is more convenient to place the sample in helium gas atmosphere.[2~5)] In gas atmosphere, the exchange of the sample is much easier. The charging on the surface of the sample under the beam bombardment which causes the high background X-radiation is much restrained, and also the partial evaporation of some volatile elements from the sample and the damage of the sample by beam heating are avoided in helium gas atmosphere. It is possible to analyze wet samples such as biological samples in gas atmosphere and to analyze even big samples using a helium gas bag.

II. EXPERIMENTAL SET UP

The experiments were carried out with the proton beam of Kyoto University cyclotron. To attain the highest sensitivity in PIXE analysis the proton energy should be chosen about 3 MeV.[6)] In the case where the proton energy is higher than 3 MeV, the background radiation induced by nuclear reaction increases rapidly. The energy of proton beam from the cyclotron is from 6 MeV to 7 MeV and the beam

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energy was reduced to 3 MeV by the energy absorption method. Figure 1 shows the helium atmosphere target chamber for PIXE analysis. The proton beam from cyclotron passed through the aluminum window of 150 micron thickness which also formed an energy absorber, and entered the helium gas atmosphere target chamber, and then went straight ahead 110 cm to the target. The total energy loss of the protons was about 4 MeV. The target was placed at an angle of 45° with respect to the beam axis. In 120° direction the X-ray detector, which was a pure-Ge detector and had a detection limit of K α–X ray of chlorine, was placed 15 cm apart from the target outside of the 9 micron mylar window of the chamber. The X-ray detection in the backward direction is preferable in consideration for the background radiation from the target.[7] The wall of the beam duct and the chamber was made of acrylic

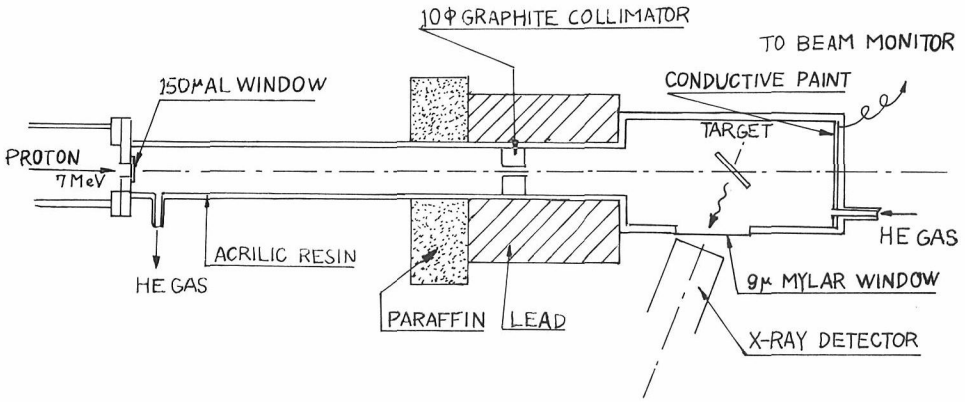

Fig. 1. Helium atmosphere target chamber.

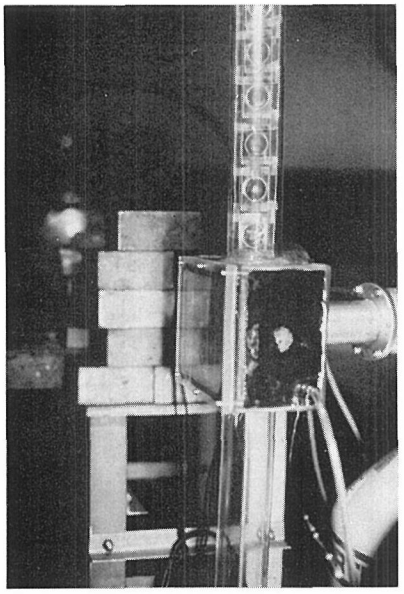

Photo. 1. Target chamber and sample changer for PIXE analysis.

resin for suppressing the production of X-ray in the wall of the duct by scattered protons. The beam was collimated by a 10 millimeter diameter graphite collimator placed at the end of the duct, and the beam diameter at the target was about 15 millimeter. The main background radiation came from the aluminum entrance window and the graphite collimator. Paraffin blocks and lead blocks were placed around the collimator for shielding the X-ray detector from the background radiation. Photo 1 shows the target chamber.

III. EXPERIMENTAL RESULTS

1) Detection Sensitivity

The detection limit of our PIXE system was determined by the following criterion; — an element is detectable if the counting for the X-ray peak of the element is three times as great as the standard deviation of the background counting.[8] The measurement value of the detection limits is given in Fig. 2. The sensitivity of our PIXE system was a little lower than others.[7] The main reason was the moderate high background γ-ray counting rate. The collimation of the proton beam from the cyclotron was quite difficult and the strayed protons collided with the wall of the beam duct and generated γ-ray by nuclear reactions.

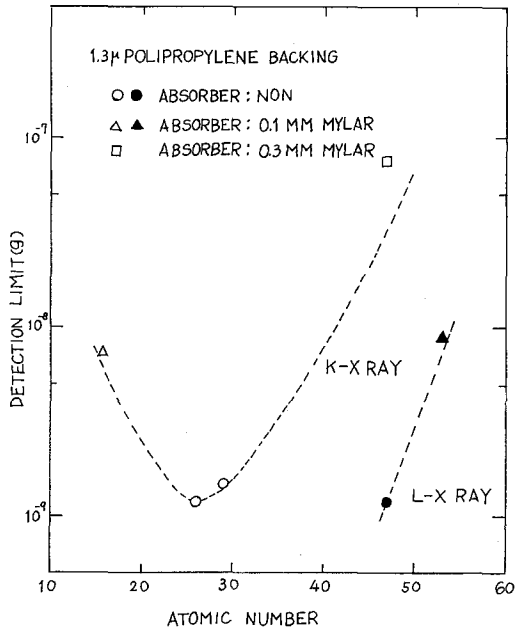

Fig. 2. Detection limit as a function of the target atomic number.

2) Applications

Application of PIXE to environmental, biological, archaeological, and electrochemical problems were performed with our PIXE system.

a) Atmospheric Aerosol in Air

For the study of air pollution problems atmospheric aerosol was analyzed by PIXE. Aerosol was collected on filter paper (TFA #41) during two hours for each sample by using an air sampler, which flow rate was 500l/min. Sampling was performed at following sites; — a streetcar line near the cyclotron laboratory (sample 1, sample 2), a street near the cyclotron laboratory where the traffic is heavy (sample 3), the front of the cyclotron laboratory (sample 4) and countryside (sample 5). The sampling was carried out from 11 a.m. to 1 p.m. for sample 1, and from 5 p.m. to 7 p.m. for sample 2 at the same place.

Figure 3 shows an X-ray spectrum from sample 3 by bombardment with protons of 3 MeV. The ratio of the concentration of elements to the value of sample 3 for four samples are given in Fig. 4. The concentration of Fe in sample 1 and sample 2 were remarkable in comparison with other samples. It is obvious that Fe came from the rails of streetcar. The highest concentration of elements except Fe in sample 3 owed to the heavy traffic on the street.

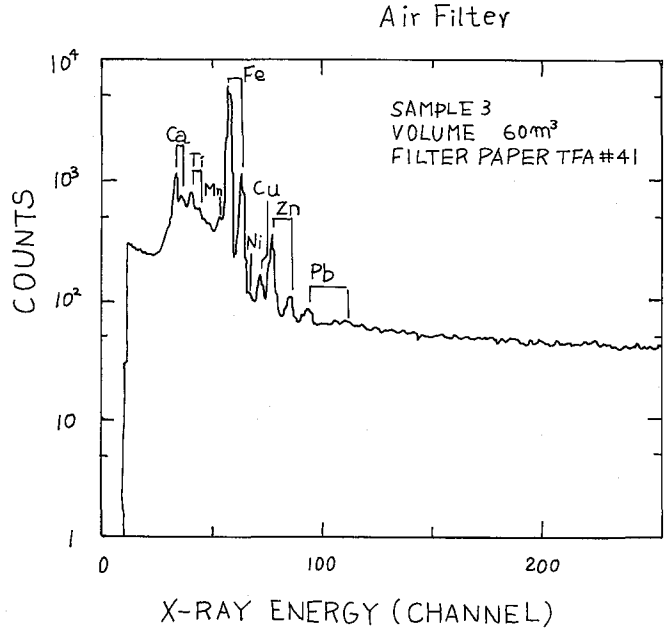

Fig. 3. X-ray spectrum from an air filter paper by bombardment with protons of 3 MeV. Aerosol was collected by using an air sampler at a street where the traffic is heavy.

b) Ginkgo Leaves

The leaves of street trees might show the good measure for the local air pollution in the town. The leaves of ginkgo trees were examined for this purpose. The leaves were washed by neutral cleanser using a soft brush and was rinsed in pure water. After drying the leaves were bombarded with the 3 MeV proton beam. Figure 5 is the X-ray spectrum of a ginkgo leaf. The ratio of concentration of K, Ca and Fe to

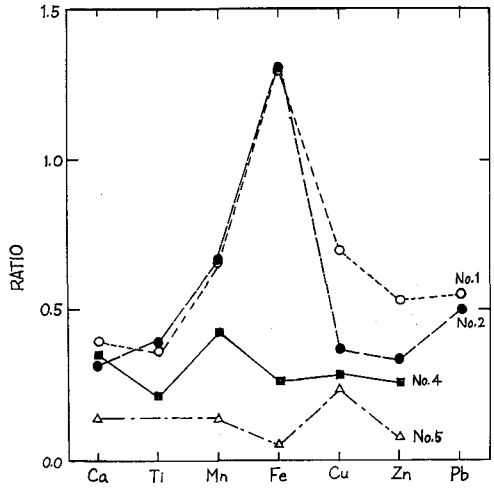

Fig. 4. Ratio of elemental concentration of aerosol to the value of sample 3 for four samples. sample 1: streetcar line (11 a.m. — 1 p.m.), sample 2: same as sample 1 (5 p.m.—7 p.m.), sample 3: heavy traffic, sample 4: cyclotron laboratory, sample 5: country-side.

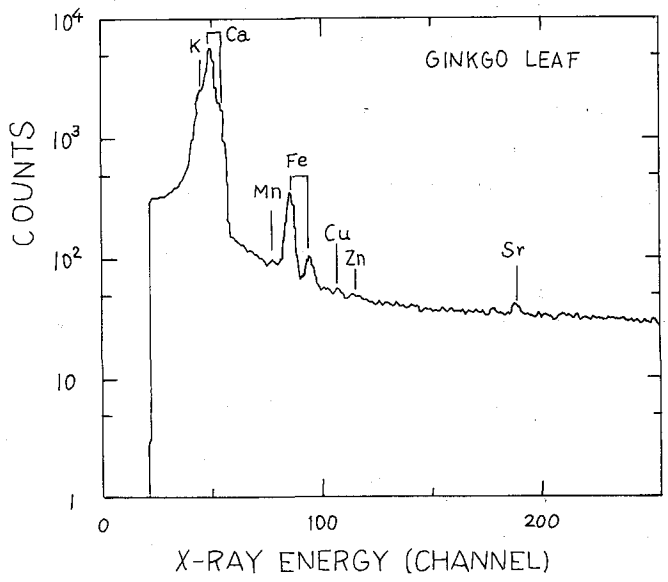

Fig. 5. X-ray spectrum of a ginkgo leaf by bombardment with protons of 3 MeV.

the value of sample No. 1 for four samples are given in Fig. 6. The high concentration of Fe was observed for the samples 1, 2 and 3 which were taken from trees in polluted sites. However notable difference of the concentration of K and Ca was not observed between the samples from polluted area (samples 1, 2 and 3) and the other (samples 4 and 5). It can be said that the concentration of Fe in ginkgo leaves shows a good

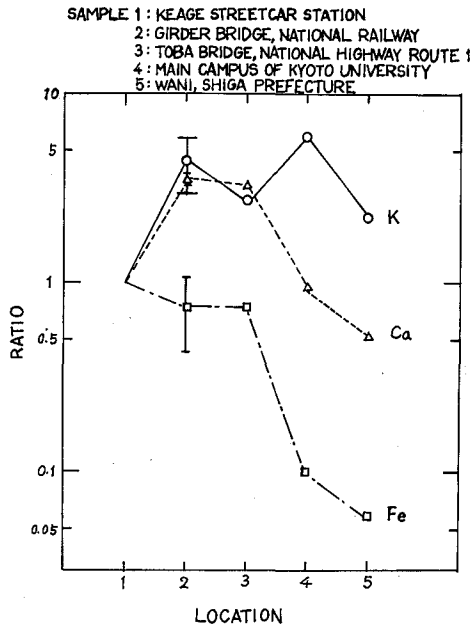

Fig. 6. Local change of elemental concentration in ginkgo leaf. The ratio of the concentration of K, Ca and Fe to the value of Sample 1 for 4 locations were plotted.

measure for the local air pollution of the town.

c) Annual Rings of a Tree

In annual rings of a tree the history of the environmental change might be recorded. The concentration of elements in annual rings of M floribunda *Takeda* tree, forty years age, was examined. The pieces of wood from different annual rings were ashed and dissolved in hot HNO_3 solution which contained Y_2O_3 as an internal standard material. After spraying the solution on the mylar film of 6 micron thickness the film was dried and was bombarded with the proton beam. The X-ray spectrum of the sample are given in Fig. 7. Figure 8 shows the annual change of Fe concentration in the rings, and Fig. 9 shows the change of concentration of elements relative to Fe. The concentration of Ca, Fe, Ni and Pb is almost constant, while the notable increase of Mn and Sr was observed in the annual rings belong to the recent year. Ti decreased in 1968, while Cu and Fe increased in that year. The sampling tree had been growing in the garden of the campus. The reason for the annual change of concentration of elements is not obvious now.

d) Rind of Fruit

PIXE analysis was examined to detect agricultural medicines remaining on rinds of fruits. The rind of fruit was bombarded with the proton beam. The X-ray spectrum from the rind of a pear is shown in Fig. 10, and the concentration of elements was given in Fig. 11. High concentration of Cu was observed in the rinds of an apple and a pear, and also high concentration of Zn was observed on the rind of a

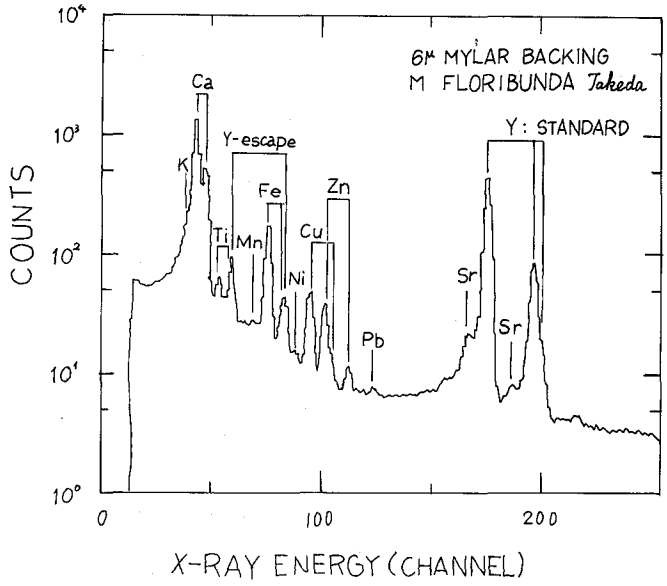

Fig. 7. X-ray spectrum of ashed wood by bombardment with protons of 3 MeV.

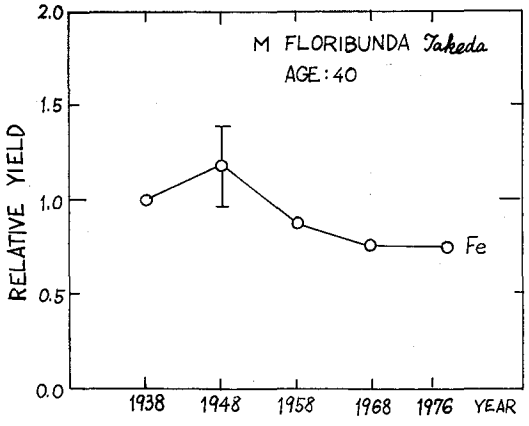

Fig. 8. Annual change of the Fe concentration in annual rings of a tree.

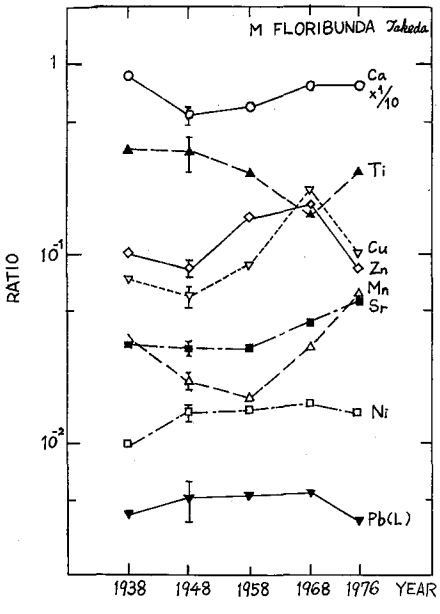

Fig. 9. Annual change of elemental concentration. The ratio of X-ray yield to the Fe K-X-ray yield for 8 elements.

pear. The elements probably came from the agricultural medicine, $CuSO_4$ or $ZnSO_4$, which was sprinkled on the surface of rind.

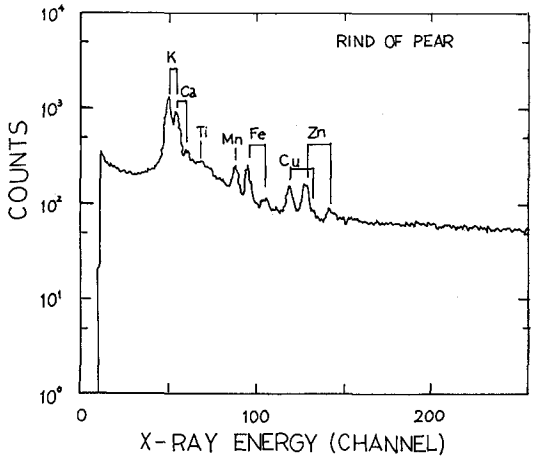

Fig. 10. X-ray spectrum from rind of a pear by bombardment with protons of 3 MeV.

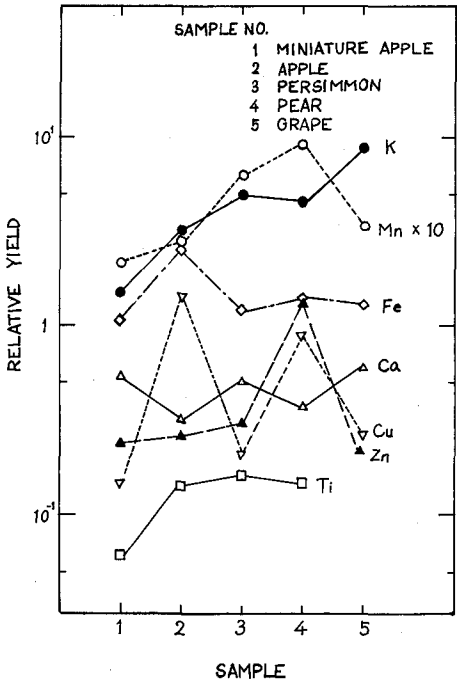

Fig. 11. Relative yield of K-X-ray from rind of fruits.

e) Human Hair

The trace elements in human hair are the good indicator for the environmental pollution and the variation of the elemental concentration might be used as a diagnostic tool.[9] Human hair were washed with acetone and were rinsed with pure water. After drying the hair were bombarded with the proton beam. Figure 12

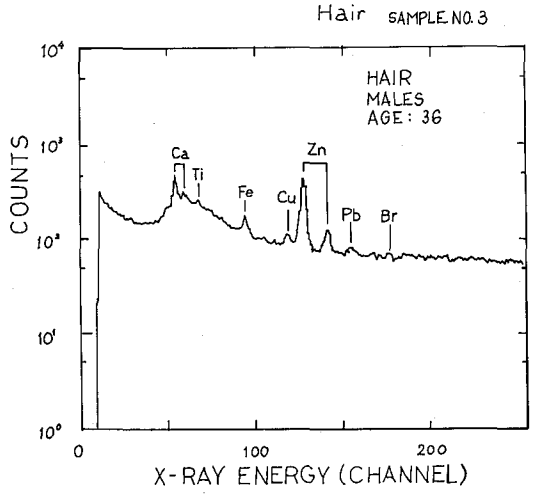

Fig. 12. X-ray spectrum from human hair by bombardment with protons of 3 MeV.

shows the X-ray spectrum from human hair. The concentration of elements is given in Fig. 13. The concentration of Zn in the hair does not change among individuals, but the trace of Pb or As was detected in samples No. 2 and No. 3.

f) Tissue of a Mouse

The element analysis of tissue might be used as a diagnostic tool.[10] The elemental concentration of muscular tissue, tumor tissue and liver tissue were compared. A slice of the tissue was sandwiched between two thin mylar films of 6μ thickness. Figure 14 shows the ratio of the elemental concentration to the value of the muscular tissue for the tumor tissue and the liver tissue. In the tumor tissue marked increase of Zn and decrease of Ti were observed. The lower concentration of Ca and Ti, and the higher concentration of Ze were observed in the liver tissue. Ni which was detected in the muscular tissue was not detected in the tumor and liver tissue. The measurements are only preliminary, and the extensive study is necessary to get the definite results about this problem.

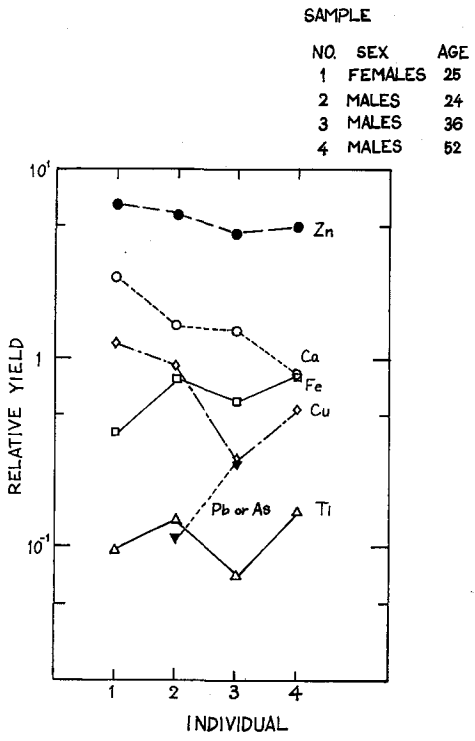

Fig. 13. Relative yield of X-ray from human hair.

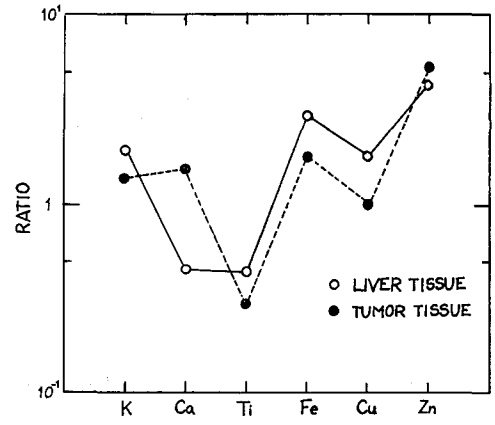

Fig. 14. Ratio of elemental concentration to the value of muscular tissue for tumor tissue and liver tissue.

g) Antique Picture

The composition of paint on an antique picture was nondestructively examined by PIXE. Photo 2 is the photograph of the antique picture. Figure 15 shows the X-ray spectrum of the white colors. It is thought the main composition of white colors is $CaCO_3$. The X-ray spectra of the red colors, golden colors and green colors are shown in Figs. 16, 17 and 18 respectively. The red colors probably contains

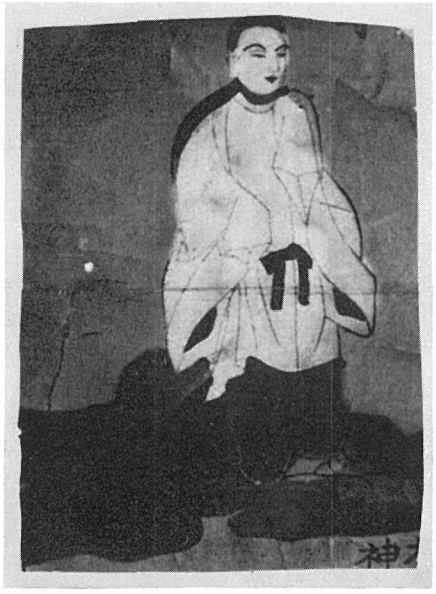

Photo. 2. Antique picture.

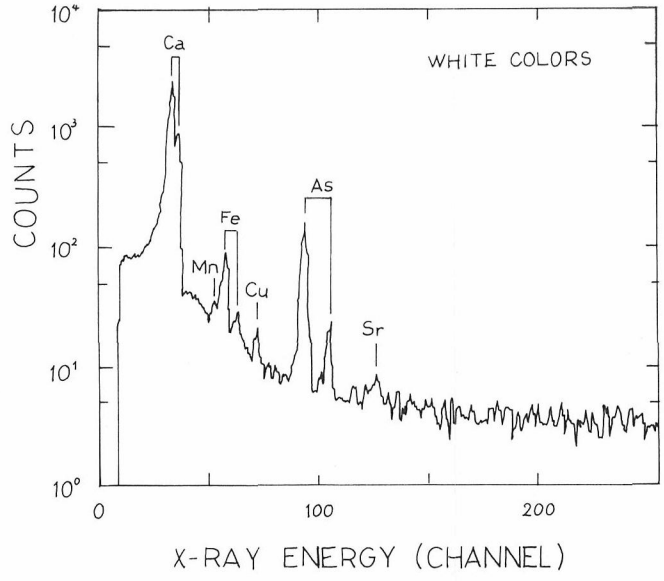

Fig. 15. X-ray spectrum from white colors painted on an antique picture by bombardment with protons of 3 MeV.

HgS and Pb_3O_4, the golden colors contains brass, and the green colors contains $Cu_3(AsO_3)_2$. It took only about five seconds to get the X-ray spectrum and the picture was scarecely damaged by the proton bombardment.

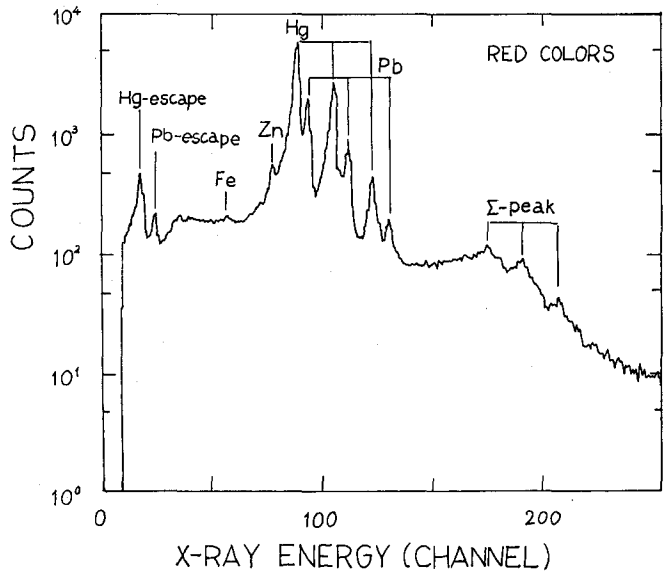

Fig. 16. Same as for Fig. 15 except colors is red.

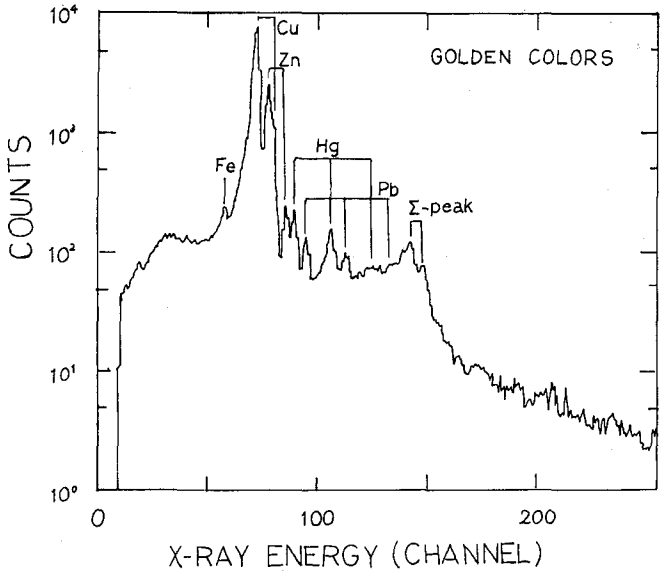

Fig. 17. Same as for Fig. 15 except colors is golden.

h) Ion-exchange resin

From electrochemical point of view it is suggested that a swollen gel of ion-exchange resins rinsed out thoroughly in distilled water holds a certain minimum amount of counter ions, the charge density of which is equal to the fixed charge density of the resin gel itself. Hence, the minimum number of the counter ions retained in the resin gel is inversely proportional to the charge number or valence of the counter ions irre-

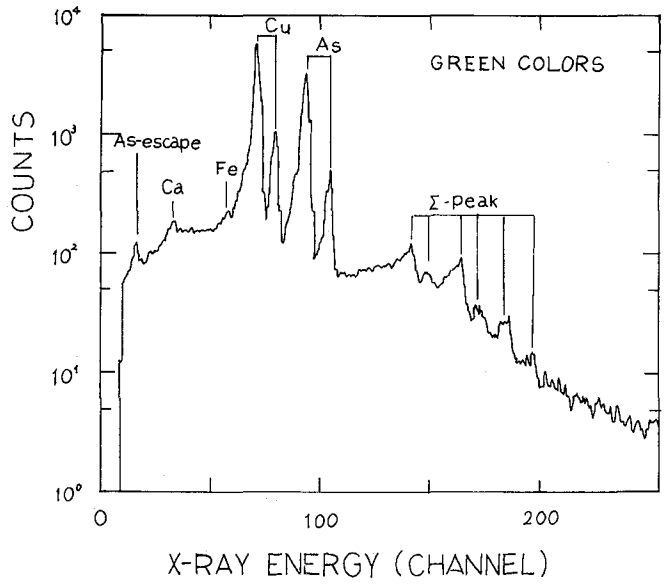

Fig. 18. Same as for Fig. 15 except colors is green.

spective of ion species. For example the number of bivalent counter ions such as Sr^{2+} retained in the resin gel is expected to be a half of that of univalent counter ions such as Rb^{+}. This relation is not confirmed yet experimentally by means of inorganic analysis especially for an ion-exchange resin Sephadex G–25, since the fixed charge

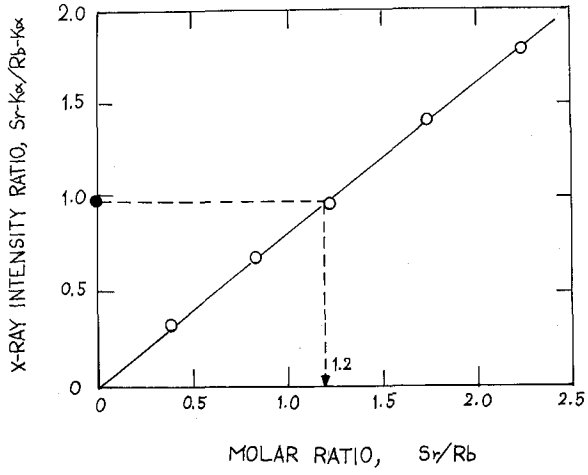

Fig. 19. Quantitative analysis of ion concentrations retained in ion-exchange resin Sephadex G–25 gels.

The solid straight line is a calibration curve obtained from observed data (○) with PIXE experiments for $SrCl_2$–RbCl solutions in known concentrations. The value for the unknown specimen of Sephadex G–25 is shown with a closed circle (●).

density in the gel (the order of 1 m equiv/dm^3) is too low to be detected with a routine means of inorganic analysis.

The present PIXE experiments can be applied to the qualitative and semi-quantitative analysis of the amount of counter ions kept in the resin gel by non-destructive means. In order to set up a calibration curve, mixed solutions of $SrCl_2$ and RbCl in various known compositions were spotted on filter papers, which were then brought to dryness. The intensity of X-rays characteristic of Sr and Rb atoms were measured for the respective filter papers prepared as above. Figure 19 is a calibration curve showing the X-ray intensity ratios of Sr–Kα to Rb–Kα against varied compositions of Sr and Rb atoms.

Next, a slurry of Sephadex G–25 retaining a minimum amount of Sr^{2+} ions and that of Rb^+ ions were mixed together in equal amount. The mixed specimen was then spread on a filter paper and was examined by PIXE method after fixation on the paper with a collodion solution. The X-ray intensity ratio of Sr–Kα to Rb–Kα for this specimen was determined to be 0.98 ± 0.05. By using the calibration curve shown in Fig. 19, the ratio of the number of Sr atoms to that of Rb atoms was estimated to be 1.2 ± 0.1 in contrast to the expected value 0.5. This marked discrepancy will cast a serious problem on electrochemical properties of ion-exchange resin gels.

IV. CONCLUSION

The PIXE analysis in helium gas atmosphere has been successfully applied to the element analysis of various samples.

The easiness of sample handling in helium gas atmosphere was ascertained. The computer facilities in the cyclotron laboratory allowed fast collection, processing and analysis of data.

It is clear that the PIXE analysis in helium gas atmosphere is a valuable and reliable tool in the analysis of trace elements in case where only small sample amounts are available and also in the analysis of wet samples such as leaf, animal tissue, paper, cloth and etc.

The authors wish to thank staffs of the Kyoto University cyclotron for operating the cyclotron, and Mr. M. Nishiki for his help during these measurements.

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